Quality Assurance Project Plan

Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds: A Study for the Washington State Department of Agriculture Conducted by the Washington State Department of Ecology

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May 2003

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Approvals

Jim Cowles, WSDA Pesticide Management Division	5.6.03 Date
Bridget Moran, WSDA Endangered Species Coordinator	5-6-03 Date
Will Kendra, Section Manager, EAP Watershed Ecology Section	5/5/03 Date
Dale Norton, Supervisor, EAP Toxics Studies Unit	5/5/03 Date
Richard Jack, Project Manager, EAP Toxics Studies Unit	5/5/03 Date
Stew Lombard, EAP Quality Assurance Coordinator	5/9/03 Date
Stuart Magoon, Director, Manchester Environmental Laboratory	5/6/2003 Date

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A. Project Management

This Quality Assurance Project Plan (QAPP) has followed USEPA guidelines for QAPP organization due to the end uses of the data by Washington State Department of Agriculture (WSDA).

A1. Distribution List

Washington State Department of Agriculture (WSDA)
Jim Cowles, Endangered Species Program
Bridget Moran, Endangered Species Coordinator

Washington State Department of Ecology, Environmental Assessment Program (EAP)
Richard Jack, Project Manager
Paul Anderson, Field Lead
Dale Norton, Supervisor, Toxics Studies Unit
Stuart Magoon, Manchester Laboratory Director
Cliff Kirchmer, Quality Assurance Officer
Will Kendra, Manager, Watershed Ecology Section

A2. Project/Task Organization

The individuals directly involved with this project and their specific responsibilities are listed below.

Jim Cowles, WSDA, Endangered Species Program (360-902-2066): End user of the data at WSDA, to be consulted or advised in all substantive decisions related to field activities, laboratory analyses, and corrective actions. Provide advice on sampling design and analytical scheme. Review and approve QAPP and subsequent revisions. Arrange for independent review of QAPP. Review project reports prepared by Ecology/EAP.

Bridget Moran, WSDA, Endangered Species Coordinator (360-902-1936): Review and approve QAPP and project reports. Track project spending. WSDA contract administrator.

Richard Jack, EAP, Toxics Studies Unit, Project Manager (360-407-6649): Overall coordination of the project and decision maker. Make revisions to draft QAPP in response to review comments. Oversee field activities, coordinate sample analysis with laboratory, and resolve problems related to these activities. Ensure QAPP implementation. Final review of data before being transmitted to WSDA and preparation of project reports.

Art Johnson, EAP, Toxics Studies Unit (360/407-6766): Prepare draft QAPP.

Paul Anderson, EAP, Toxics Studies Unit, Field Lead (360-407-7548): Prepare for and conduct field work. Assist with QAPP and project reports. Responsible for implementing QAPP protocols and requirements for field work. Ecology's Environmental Information Management (EIM) database entry.

Carolyn Lee, EAP, Toxics Studies Unit (360-407-6430): Environmental Information Management (EIM) data entry technical support.

Dale Norton, EAP, Toxics Studies Unit Supervisor (360-407-6765): Review and approve QAPP and project reports. Track project milestones and spending.

Stew Lombard, EAP, QA Coordinator (360-895-6148): Review and approve QAPP and subsequent revisions.

Stuart Magoon, EAP, Manchester Laboratory Director (360-871-8801): Review and approve QAPP. Coordinate and schedule laboratory analyses, data review, and validation.

John Weakland, EAP, Manchester Laboratory (360-871-8820): Organics Unit supervisor. Review and approve QAPP.

Gregory Perez, EAP, Manchester Laboratory (360-871-8820): Pesticide analyst.

Bob Carrell, EAP, Manchester Laboratory (360-871-8804): Pesticide/Herbicide analyst.

Will Kendra, EAP, Manager Watershed Ecology Section (360-407-6698): Review and approve QAPP. Policy review of project reports.

A3. Problem Definition/Background

The Washington State Pesticide/Endangered Species Act (ESA) Task Force was convened in March of 2000 to address the considerable scientific uncertainty surrounding the effects of pesticides on the essential biological requirements of salmonids. The task force is a collaborative effort between the National Marine Fisheries Service; the U.S. Fish and Wildlife Service; the Environmental Protection Agency (Region 10); and the Washington State Departments of Agriculture (WSDA), Ecology, Fish and Wildlife, and Natural Resources. A primary goal of the task force has been to develop an evaluation process that incorporates the best available scientific data and information on 1) the transport of pesticides to salmonid habitat and 2) the toxicity of these chemicals to fish and/or the aquatic food web (from *A Process for Evaluating Pesticides in Washington State Surface Waters for Potential Impact to Salmonids*, Washington State Pesticide/ESA Task Force, September 2001). Since the task force's formation, litigation involving Washington Toxics Coalition vs. USEPA has occurred which resulted in a summary judgment against USEPA requiring consultation under the Endangered Species Act for 54 pesticides.

A key question being asked by the task force is "Is there evidence of exposure of salmonids or the prey base?" The task force concluded the data sets available for answering this question are incomplete and has identified "a need for increased surface water monitoring that reflects current land use patterns/practices as they relate to salmonid habitat and biology." The task force recommended the following WRIAs for pesticide monitoring: the Lower Skagit (#3), Lower Yakima (#37), Lower Crab Creek (#41) and Walla Walla (#32) representing the agricultural basins; the Cedar-Sammamish (#8), representing an urban basin.

WSDA and Ecology have entered into an interagency agreement providing funding to Ecology to conduct a surface water monitoring program for pesticide residues in salmonid habitat in Washington State. WSDA will use these and other available pesticide data to: 1) Assist EPA in developing exposure assessments for pesticides in Washington State surface waters to evaluate the potential risk to T/E salmonids and 2) measure performance of any actions put in place to mitigate/minimize the transport of pesticides to surface waters.

A4. Project/Task Description and Schedule

The purpose of this project is to conduct a surface water monitoring program for pesticide residues in salmon habitat in two index watersheds in Washington State. As described in section B1, WSDA and EAP have selected the lower Yakima and Cedar-Sammamish basins for monitoring (Figure 1). A wide range of pesticides including organochlorines (OC), organophosphates (OP), nitrogen-containing (N), chlorinated herbicides, and carbamates will be analyzed at the parts per billion-to-parts per trillion level (Appendix A). Some additional organic compounds will be analyzed in Thornton Creek to evaluate potential confounding chemicals (Appendix B). The monitoring effort will focus on those periods with greatest potential for pesticide transport to surface waters.

The sampling program and laboratory analyses will be conducted by Ecology's Environmental Assessment Program (EAP). EAP will provide the data to WSDA in annual reports and electronically. EAP will enter the data into Ecology's Environmental Information Management (EIM) database.

Field work for this project will begin the second week of April 2003. Funding is scheduled through June 2005. The samples will be analyzed at or through Ecology's Manchester Laboratory. The project schedule is shown below.

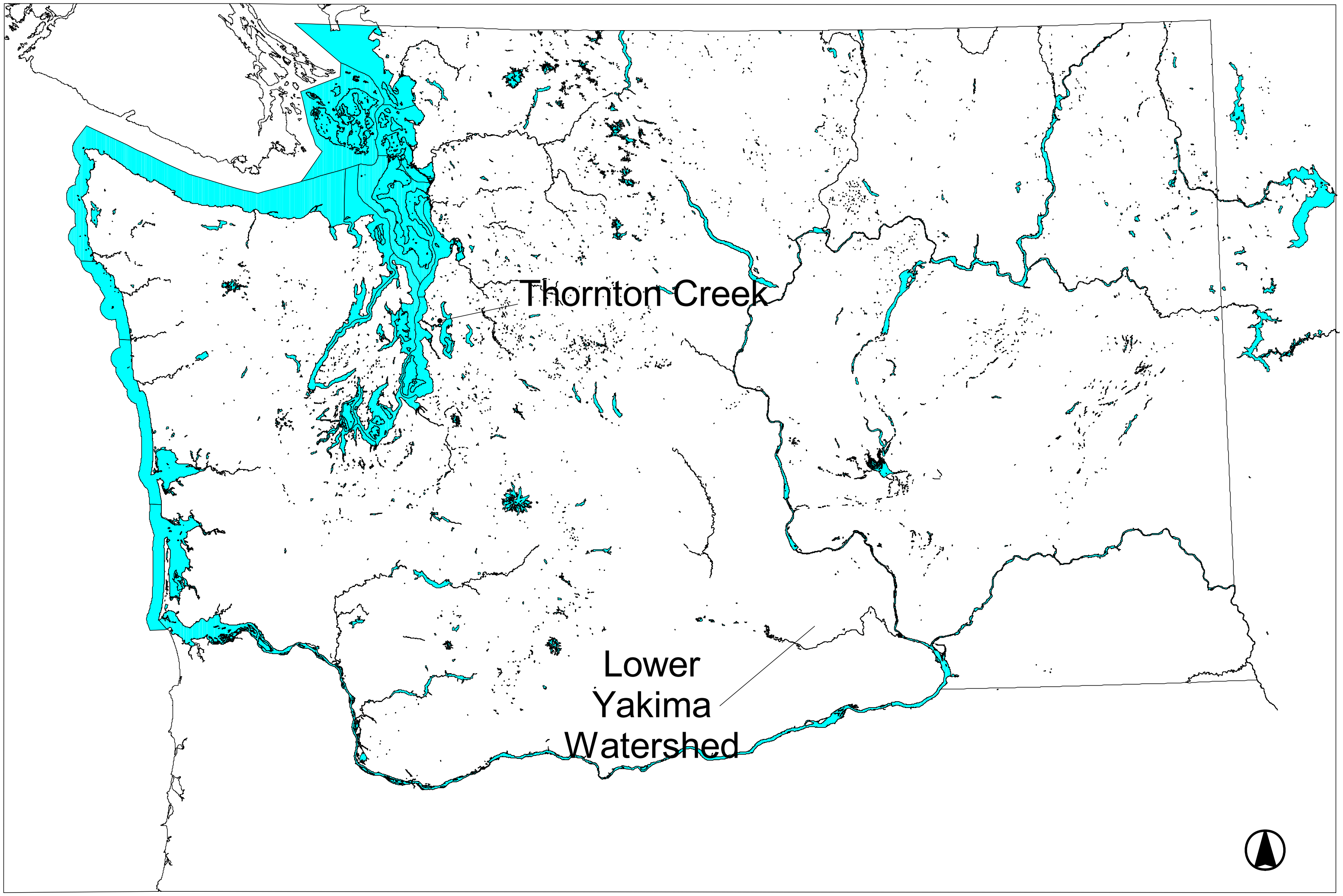


Figure 1. WSDA pesticide sampling watersheds.

SCHEDULE												
	FY03				FY04							
	03										04	
	M	A	M	J	J	A	S	O	N	D	J	F
Draft QAPP (3/14)												
Sampling Approval (3/31)												
Field Work/Lab Analyses		Y/ C	Y/ C	Y/ C	Y	Y	Y	Y/ C	C	C		
	FY04				FY05							
	04										05	
	M	A	M	J	J	A	S	O	N	D	J	F
Annual Report (<u>2003-4</u>)	Y/ C											
Field Work/Lab Analyses		Y/ C	Y/ C	Y/ C	Y	Y	Y	Y/ C	C	C		
	FY05				FY06							
	05										06	
	M	A	M	J	J	A	S	O	N	D	J	F
Annual Report (<u>2004-5</u>)	Y/ C											
Field Work/Lab Analyses		Y/ C	Y/ C	Y/ C								
Annual Report (<u>2005</u>)								Y/ C				

Y = Yakima watershed
C= Cedar-Sammamish watershed

Ecology EIM Data Entry Due Dates

Annual 2003-4	March 2004
Annual 2004-5	March 2005
Annual 2005	October 2006

<u>A5. Quality Objectives and Criteria for Measurement Data</u>

The project data quality objective (DQO) is to provide WSDA with valid data off known and documented quality for identifying pesticides that do and do not pose a risk to salmonids. Data quality indicators and associated measurement performance criteria for this project are identified in Table 1.

Table 1. Data Quality Indicators and Measurement Performance Criteria for Pesticides

Data Quality Indicator	Measurement Performance Criteria	QC Sample Used to Assess Measurement Performance	QC Sample to Assess Error for Sampling (S) Analytical (A) or both (SA)
Precision	≤ 50% RPD	MS/MSD	A
	≤ 50% RPD	field replicates	SA
Bias	50-150% recovery*	MS/MSD, LCS	A
	50-150% recovery	surrogate spikes	A
	< RL	method blanks	A
	< RL	field blanks	S
	50-150% recovery	field spikes	S

*20-150% for chlorinated herbicides
RPD = relative percent diffrence
RL = Reporting limit
MS/MSD = Matrix spike/Matrix Spike Duplicate
LCS= Laboratory Control Sample

Table 2 summarizes the practical quantitation limits (PQL) that Manchester Laboratory is able to achieve using the analytical methods described in this QAPP. PQLs vary with the matrix and pesticide being analyzed. Results from other recent monitoring programs conducted by EAP show that PQLs for the majority of pesticides being analyzed for the present study are at the low end of the range shown in Table 2.

Table 2. Manchester Laboratory Practical Quantitation Limits

Analysis	Analytical Method	PQL
OC pesticides	GC/AED EPA 3510/8085	0.01 - 0.1 ug/L
OP pesticides	GC/AED EPA 3510/8085	0.01 - 1 ug/L
N pesticides	GC/AED EPA 3510/8085	0.01 - 1 ug/L
Chlorinated herbicides	GC/AED EPA 1658/8085	0.08 - 1 ug/L
Carbamates	HPLC EPA 8318	0.1 - 5 ug/L
TSS	EPA 160.2	1 mg/L
BNA Organics	Capillary GC/MS, EPA 8270	1 to 5 ug/L

Water quality criteria for pesticides are generally ten times higher than the lower end of the PQL range (NAS, 1973; CCREM, 1987; Norris and Dost, 1991; Driver, 1994; WAC 201A; EPA, 2002). Therefore, the level of sensitivity afforded by the analyses proposed here should be adequate to evaluate the potential risk that most of the target pesticides pose to salmonids or their prey.

The PQLs associated with the bioaccumulative insecticides chlordane, DDT, and heptachlor will not be low enough to determine compliance with chronic water quality criteria. This is not considered a significant shortcoming in that these chemicals are no longer used and the chronic criteria are for protection of higher predators. Also, substantial amounts of low-level data already exist for these compounds, especially in the lower Yakima drainage (Joy and Patterson, 1987; Rinella et al., 1999; Ebbert and Embrey, 2002). Studies have shown that chlorinated insecticides are rarely detected in western Washington streams (Davis, D. 1993; Davis et al., 1998; other Washington State Pesticide Monitoring Program reports by Davis; Voss and Embrey, 2000).

The data for this project must accurately and precisely represent conditions existing at the time of sample collection. Representativeness will be addressed by collecting the samples as described in this document. Field or laboratory conditions that may affect sample integrity will be documented in field logs or in laboratory case narratives.

Individual data sets must be comparable in order that results can be combined for decision making. Comparability will be addressed by consistently collecting, analyzing, and reporting the data as described in this document.

The completeness goal for valid data is 95% for this project.

A6. Special Training Requirements/Certification

No special training requirements or certifications are required for this project except for Washington State Department of Labor and Industries required first aid/CPR and EAPs safety manual procedures training. Information concerning the personnel qualifications for individuals performing this work is on file at Ecology Headquarters.

A7. Documentation and Records

This information is covered by the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0. Field logs will be maintained in the project files at EAP.

B. Measurement/Data Acquisition

B1. Sampling Process Design (Experimental Design)

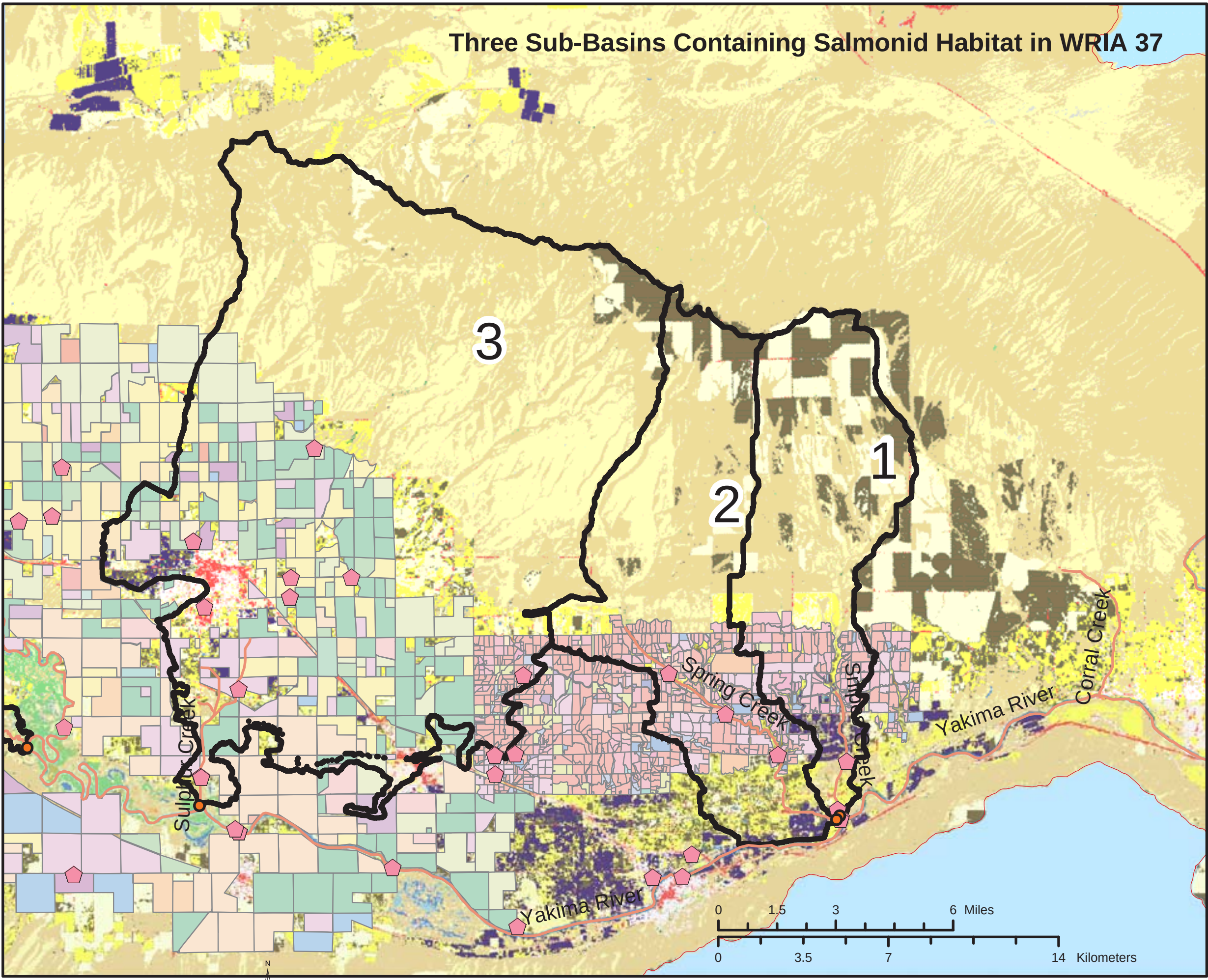
Both selected watersheds are utilized by populations of listed or depressed stock salmonids. Salmonid habitat restoration activities have occurred or are planned in both watersheds. Because of the variety of crops grown and pesticides used, the lower Yakima was selected among the four agricultural basins the task force had recommended for pesticide monitoring. GIS was used to analyze cropping patterns (WSDA and Benton County Conservation District databases), historical pesticide detections (Ecology and USGS monitoring data referenced elsewhere), and salmonid habitat (Salmon and Steelhead Stock Inventory). Based on this analysis, three lower Yakima creeks were selected for monitoring: Marion Drain, Sulphur Creek, and Spring Creek. The criteria for selecting these sub-basins were the percent area cropped and the diversity of crops in the drainage. An example of the overlay of these GIS coverages for Sulphur and Spring Creeks is shown in Figure 2. Appendix C provides watershed statistics.

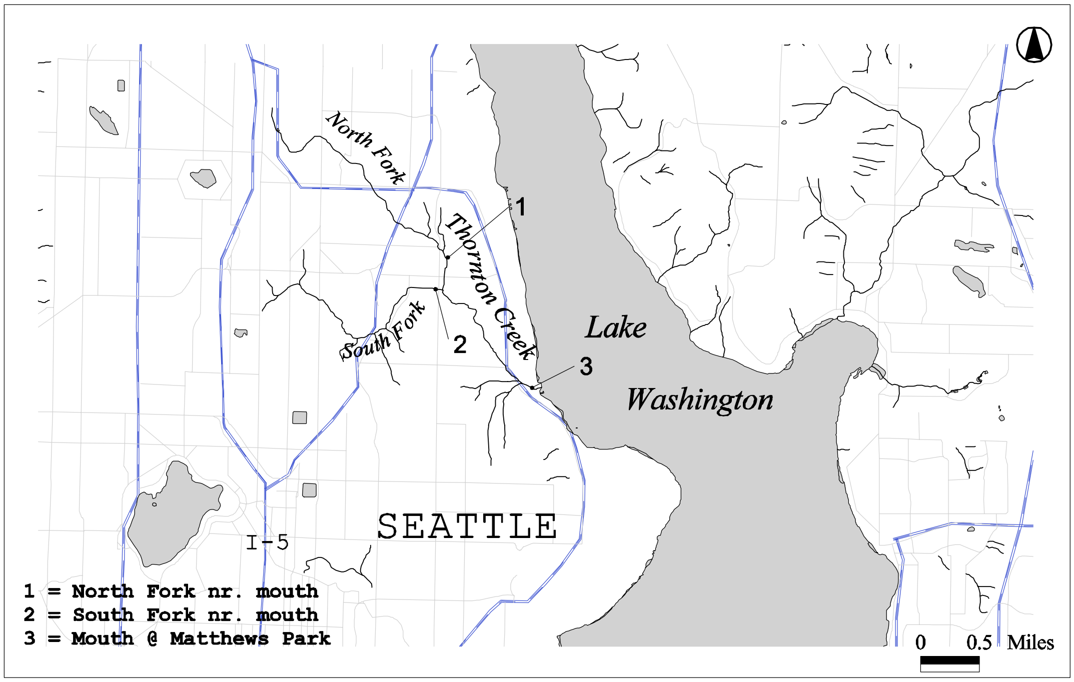
The task force recommended monitoring a watershed in the Cedar-Sammamish basin to obtain data on pesticides from urban land use. Thornton Creek was selected for monitoring in consideration of its high population density and income levels, large amount of impervious surface (60-70%), historical pesticide detections, and salmonid habitat. The Washington State Department of Fish and Wildlife has an interest in Thornton Creek being monitored in light of recurring fall kills and low productivity of coho salmon (Timothy Quinn, Chief Habitat Scientist, Personal Communication).

Given the requirement to analyze a large number of the chemicals currently in use, the budget allowed for collection of approximately 120 – 130 field samples each fiscal year. Due to the diversity of crops and subsequent variety of pesticides used for crop protection, more emphasis was placed on agricultural basins.

Nine monitoring stations are proposed, as shown in Figures 3 and 4 and Table 3: two on Marion Drain, one on Sulphur Creek, three on Spring Creek, and three on Thornton Creek. All sites lie within utilized or potential salmonid habitat. The sampling effort in Yakima basin streams is proportional to the amount and quality of habitat in each drainage. The Cedar-Sammamish basin sampling is being focused on a single creek, based on the assumption that pesticide use is similar among urban watersheds.

Figure 2. A GIS Analysis of Sulphur (3), Spring (2), and Snipes (1) Creeks (Jim Cowles, WSDA). [Legend unavailable; salmonid habitat highlighted in red, historical pesticide sampling sites shown as pentagons]





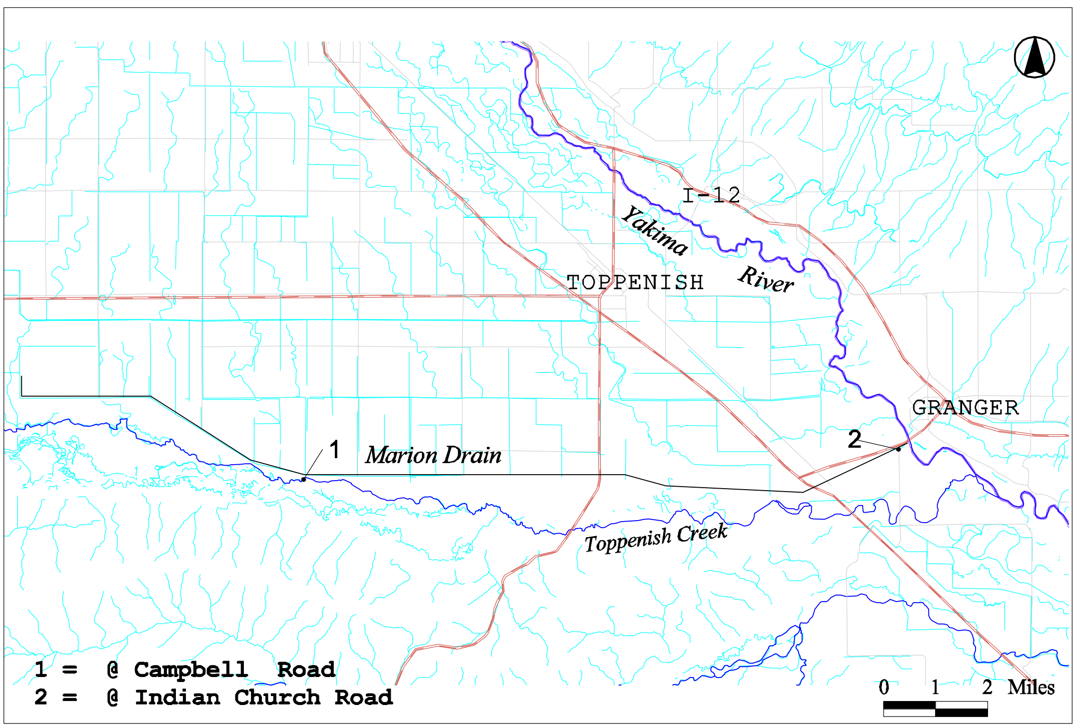


Figure 3. Monitoring Stations on Thornton Creek and Marion Drain

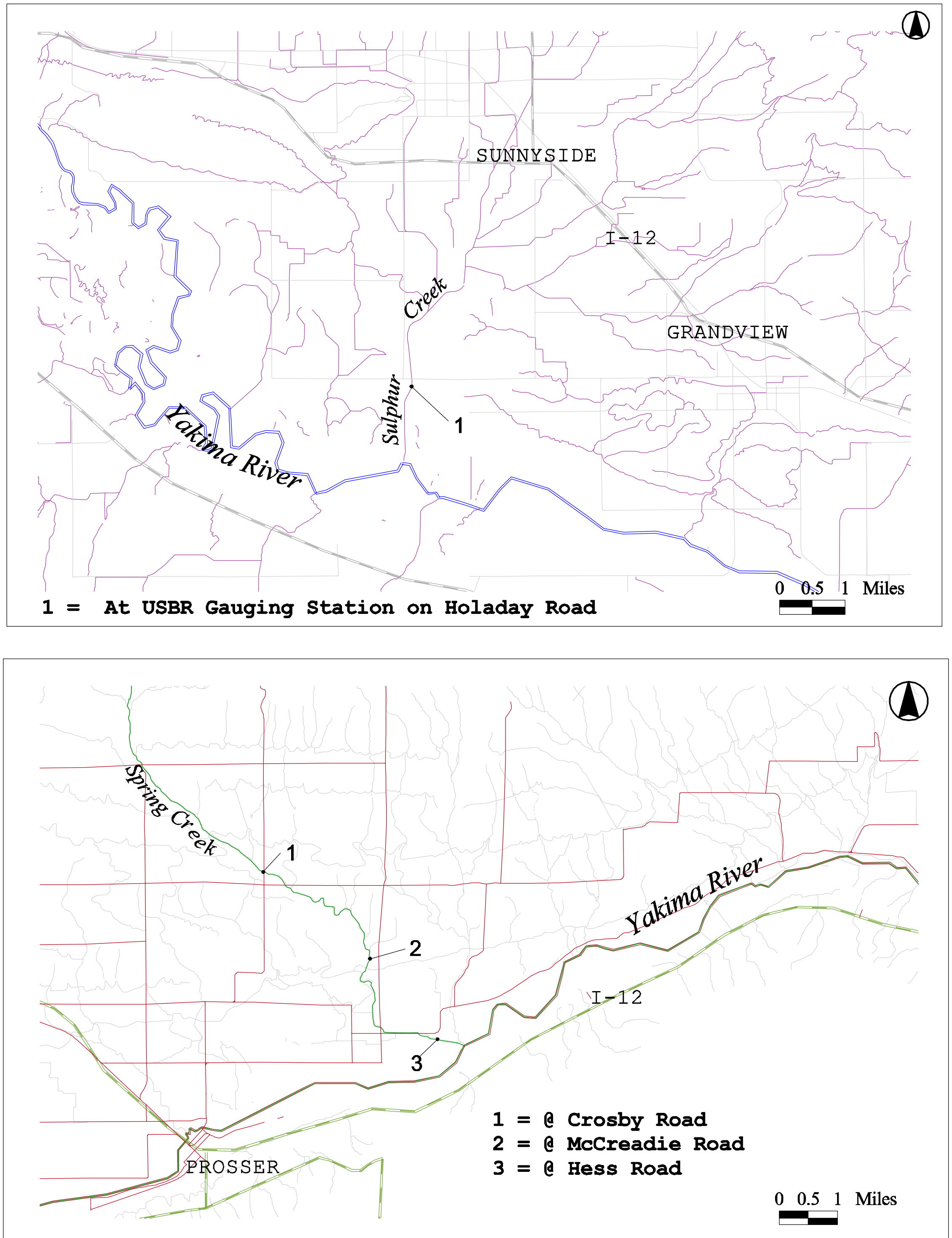


Figure 4. Monitoring Stations on Sulphur and Spring Creeks

Table 3. Pesticide Monitoring Stations

Creek/Drain	Station Location	Drainage Area (sq. miles)	Previous Sampling
Yakima Basin			
Marion Drain	Nr. mouth @ Indian Church Road	~100	1,2,3
"	@ Campbell Road	- -	
Sulphur Creek	Nr. mouth @ McGee Road	160	1,2,3,4,5
Spring Creek	Nr. mouth @ Hess Road	- -	1,2,3,4,5
"	@ McCreadie Road	34	
"	@ Hanks Road	- -	
Cedar-Sammamish Basin			
Thornton Creek	Nr. mouth @ Matthews Park	11.3	7,8
"	North Fork nr. mouth	3.1	6
"	South Fork nr. mouth	3.4	6

1 = Johnson et al. (1986) 2 = Rinella et al. (1992)
3 = Ebbert and Embrey (2002) 4 = Davis et al. (1998)
5 = Joy and Patterson (1997) 6 = Voss and Embrey (2000) 7 = Davis (1993)
8 = USGS unpublished routine monitoring data since 1996

Pesticide monitoring of surface waters in Washington State and elsewhere has shown that the majority of detections and highest concentrations occur during or shortly after application and during runoff events (Davis, 1993; Davis et al., 1998; Wagner et al., 1996; Voss and Embrey, 2000). Groundwater can be a significant source of certain pesticides during low-flow conditions in agricultural areas, for example the herbicide atrazine (Wagner et al., 1996). For a variety of watersheds statewide, Pitz and Sinclair (1999) estimated low streamflow groundwater contributions at between 69 and 86 percent of annual streamflow.

Therefore, the WSDA/EAP monitoring program for the lower Yakima will focus on the irrigation season, with weekly monitoring at all stations during the spring--when the heaviest pesticide applications occur--and biweekly monitoring at the most downstream station in each drainage continuing into the late summer/early fall low-flow period. A similar weekly monitoring schedule will be followed to cover the spring application period in Thornton Creek. Monitoring of Thornton Creek will stop after June and resume at all stations in the fall where it will be timed to coincide with runoff events.

Table 4 shows the proposed distribution of sampling effort and an estimate of laboratory costs. Due to budget constraints, fewer sites will be sampled in spring 2004 and the pesticides monitored for will be reevaluated after this summer's sampling has concluded. The spring 2004 monitoring program may be further modified from what is shown, based on the monitoring data. OC pesticides will be analyzed in Thornton Creek, but only in alternate weeks. In the other weeks, some semi-volatile organics (BNA organics) common in urban runoff will be analyzed. These constituents will be monitored every other week during the spring 03 sampling and during the fall 03 sampling in Thornton Creek. These analyses will be used to evaluate the degree to which non-target compounds might interfere with the pesticide analysis or potentially confound pesticide residue interpretations. The sampling design for FY05 has yet to be determined, although modifications will be based upon FY03 and FY04 results.

Table 4. Number of Samples Planned and Estimate of Laboratory Costs, FY03 - FY05. Lab prices incorporate a discount for base funding.

FY03

Spring Intensive 2003: 6 sites on 3 Yakima creeks, 3 Thornton Creek sites, every week April-June

Analysis	Cost	Sites	Visits	Samples	Field Blank	Replicates	MS/MSD	N=	Subtotals
OC pest.	184	9	11	99	2	8	12	121	22,264
OP pest.	184	9	11	99	2	8	12	121	22,264
N pest.	194	9	11	99	2	8	12	121	23,474
Chlor. herb.	184	9	11	99	2	8	12	121	22,264
Carbamates	186	9	11	99	2	8	12	121	22,506
TSS	10	9	11	99	0	8	0	107	1,070
BNA SVOCs	253	3	5	15	2	5	10	32	8,096
Field Spikes	660	- -	- -	3	0	0	0	3	1,980
							Total FY03 =		$123,918

FY04

Remainder 2003 Irrigation Season: Mouth of 3 Yakima creeks, every other week, July - October

Analysis	Cost	Sites	Visits	Samples	Field Blank	Replicates	MS/MSD	N=	Subtotals
OC pest.	184	3	8	24	2	4	8	38	6992
OP pest.	184	3	8	24	2	4	8	38	6992
N pest.	184	3	8	24	2	4	8	38	6992
Chlor. herb.	184	3	8	24	2	4	8	38	6992
Carbamates	186	3	8	24	2	4	8	38	7068
TSS	10	3	8	24	0	4	0	28	280
								Subtotal=	$35,316

FY04

Fall/Winter Runoff 2003: 3 Thornton Creek sites, 2 samples per site, 3 runoff events, October-December

Analysis	Cost	Sites	Visits	Samples	Field Blank	Replicates	MS/MSD	N=	Subtotals
OP pest.	184	3	6	18	1	3	6	28	5152
N pest.	184	3	6	18	1	3	6	28	5152
Chlor. herb.	184	3	6	18	1	3	6	28	5152
Carbamates	186	3	6	18	1	3	6	28	5208
BNA SVOCs	253	3	6	18	1	3	6	28	7084
TSS	10	3	6	18	0	3	0	21	210
								Subtotal=	$27,958

FY04 (continued)

Spring Intensive 2004: 4 sites on 3 Yakima creeks, 2 Thornton Creek sites, every week April-June

Analysis	Cost	Sites	Visits	Samples	Field Blank	Replicates	MS/MSD	N=	Subtotals
OC pest.	184	4	12	48	2	5	8	63	11,592
OP pest.	184	6	12	72	2	5	8	87	16,008
N pest.	184	6	12	72	2	5	8	87	16,008
Chlor. herb.	184	6	12	72	2	5	8	87	16,008
Carbamates	186	6	12	72	2	5	8	87	16,182
TSS	10	6	12	72	0	5	0	77	770
								subtotal =	$76,568
								Total FY04 =	$132,928

FY05

Sampling design to be determined; approximately 130 field samples anticipated

Laboratory budget = $127,461

The extent to which this sampling program will provide the exposure data that the Task Force requires can be gauged from the life history of some of the salmonid species that inhabit these watersheds (Table 5). Although the present plan does not call for pesticide data to be collected year around, the periods not being sampled either coincide with low pesticide use and greater dilution during the winter months or reduced surface runoff during the summer (Thornton Creek).

Table 5. Life History Summaries for Some Salmonid Species in the Yakima and Cedar-Sammamish Basins Compared to Timing of Pesticide Monitoring
pesticide sampling (X), freshwater entry (fw), spawning (sp), freshwater rearing (stipled) =

Basin/Species	A	M	J	J	A	S	O	N	D	J	F	M
Lower Yakima	X	X	X	X	X	X	X					
Summer Steelhead[2,3]	sp					fw	fw	fw	fw	fw	sp	sp
Fall Chinook[1]					fw	fw	sp	sp	sp			
Spring Chinook[2]	fw	fw	fw		sp	sp	sp					
Cedar-Sammamish	X	X	X				X	X	X			
Winter Steelhead[2]	fw/sp							fw/sp	fw/sp	fw/sp	fw/sp	fw/sp
Chinook[3]					fw	sp	sp					
Coho						fw	fw/sp	fw/sp	fw/sp	fw/sp	fw/sp	
Sockeye[2]			fw	fw	fw	sp	sp	sp				

[1]healthy [2]depressed [3]threatened [4]critical

(SaSSI, 1992)

B2. Sampling Methods Requirements

Pesticide sampling methods will follow routine EAP procedures described in Davis (1992). Sampling methods for conventional parameters and methods for measuring field parameters will follow the EAP guidance in Cusimano (1993) and Ward (2001).

When water depths are less than one foot, water samples will be collected as simple grabs from quarter-point transects. A hand-held one-quart glass bottle, cleaned to EPA (1990) QA/QC specifications, will be used to collect the samples. Each quarter-point grab will be split among appropriate containers for each analysis and grab sampling will continue until acceptable sample volumes are achieved (see section B3). When water depths are greater than one foot, a DH-81 depth integrating bridge sampler will be used. The DH-81's glass bottle and polyethylene nipple will be cleaned as above.

Field personnel collecting the samples will wear non-talc, nitrile gloves. Every reasonable effort will made to avoid introducing dirt, dust, or other contaminants into the samples.

Field blanks, replicates samples, and spiked samples will be collected or prepared as described in section B5. The frequency of these field QC samples is shown in Table 4. Extra sample volumes will be collected for matrix spikes and matrix spike duplicates (see section B5).

A label will be placed on each sample indicating project name, station, assigned laboratory sample number, collection date, and analysis required. The pesticide samples will be enclosed in bubble-wrap and all samples will be placed on ice immediately upon collection. The samples will be returned to Ecology HQ and held in a secure cooler for transport to Manchester Laboratory within one-to-two days of collection. Sample holding times will be observed (see section B3) and chain-of-custody maintained.

An Orion 250A meter and a Beckman model RB-5 conductivity bridge or equivalent meters will be used for field measurements of pH and conductivity, respectively. The pH meter will be calibrated each day with pH 4 and pH 10 standards and a pH 7 buffer will be used as a check standard each time the instrument is used. Temperature will be measured with a precision thermometer or meter.

Flow data will be obtained from existing gauges operated by the U.S. Bureau of Reclamation and U.S. Geological Survey (Yakima watershed), King County Department of Natural Resources (Cedar-Sammamish watershed), or measured directly with a Marsh-McBirney or Swoffer flow meter and top-setting rod. Flow will be determined using USGS procedures (Rantz et al. 1982). Station positions will be recorded with a hand-held GPS.

To ensure successful completion of each sampling event, extra sample bottles, spare parts, extra batteries, backup meters, and other needed sampling gear will be carried along for each field collection.

Available safety gear will include chemical goggles, personal floatation devices, and a 50' length of floating line. Field personnel will wear knee, hip, or chest waders depending on water depths.

B3. Sample Handling and Custody Requirements

Sample containers, preservation, and holding times will be as described in Table 6. Sample containers will be obtained from Manchester Laboratory or contract laboratory selected by the Manchester Laboratory.

Table 6. Field Procedures

Parameter	Min. Sample Size	Container	Preservation	Holding Time until extraction
OC pesticides, OP pesticides, Nitrogen pesticides,	1 gallon	1 gal. glass[a]	Cool to 4^oC	7 days
Chlorinated herbicides	1 gallon	1 gal. glass[a]	Cool to 4^oC	7 days
Carbamates	1 L	1 L amber glass[a]	MCA buffer, 4^oC	28 days
BNA Organics	1 gallon	1 gal. glass[a]	Cool to 4^oC	7 days
TSS	1000 mL	1 L poly bottle	Cool to 4^oC	7 days

[a]Organic-free with Teflon lined lides, with certificate of analysis.

Pesticides in current use will receive the highest priority for extraction and analysis within the holding times. If holding times must be broken, pesticides not in current use will receive lower priority extraction and analysis.

Chain-of-custody procedures, field documentation, and sample tracking will be in accordance with the Manchester Laboratory Users Manual, July 2002. Date and time of collection, location, sample size, laboratory sample number, location coordinates, flow measurements/gauge readings, and field observations will be recorded in ink on a field log. Each sheet of the field log will be initialed in ink by the sample collector.

B4. Analytical Methods Requirements

The samples will be analyzed by Manchester Laboratory, except for carbamates which will be analyzed by a contract laboratory selected by the Manchester Laaboratory. Table 7 shows the types and numbers of samples to be analyzed, expected range of results, and analysis methods proposed. Other methods may by used by the Manchester Laboratory after consulting with the EAP project lead.

Table 7. Laboratory Procedures

Analysis	Approx. Number of Field Samples* FY03	FY04	FY05	Expected Range of Results	Analytical Method	Manchester SOP
OC pesticides	118	101	101	0.01 - 0.1 ug/L	GC/AED EPA 3510/8085	73085/-01
OP pesticides	118	131	131	0.01 - 0.5 ug/L	GC/AED EPA 3510/8085	73085/-01
Nitrogen pesticides	118	131	131	0.01 - 0.5 ug/L	GC/AED EPA 3510/8085	73085/-01
Chlorinated herbicides	118	131	131	0.08 - 5 ug/L	GC/AED EPA 1658/8085	730071/-01
BNA Organics	60	0	0	1 - 10 ug/L	GC/MS EPA 8270	730011
Carbamates	118	131	131	0.1 - 1 ug/L	HPLC EPA 8318	73003
TSS	118	131	131	1- 100 mg/L	EPA 160.2	710052 v 2.3

*including field QC samples

Reporting limits will be as shown in the Manchester Laboratory Users Manual, July 2002. Reporting limit requirements for this project are discussed in section A5 of this QAPP. Manchester will report at the lowest level consistent with the methods used.

The pesticides and breakdown products to be analyzed are listed in Appendix A. The list includes two compounds that are not part of Manchester's routine schedule: the N-pesticide propargite; the OC pesticides, captan, and kelthane (dicofol); and the carbamates, dioxacarb, and promecarb.

If problems are encountered in analyzing the samples, the EAP project lead will be consulted at the earliest opportunity. Manchester's normal turn-around time of 30-45 days will meet the needs of this project. Excess sample extracts will be saved for a period of 60 days after reporting the data to the project lead.

The overall implementation of the quality assurance program at the laboratory is addressed in the Manchester Laboratory Quality Assurance Manual.

B5. Quality Control Requirements

The field QC samples to be analyzed for this project are shown in Table 4. The recommended location and timing of these samples are shown in Table 8.

Table 8. Number, Location, and Timing of Field QC Samples

	Yakima Creeks			Thornton Creek		
Sampling Period	Number	Location	Timing	Number	Location	Timing
Spring Intensive, April - June 2003						
Transfer blanks	1	unspecified	first collection	1	unspecified	May
Replicate samples	6	1 per station	~biweekly	2	unspecified	unspecified
Field Spikes	3	unspecified	April	0	- -	- -
Remainder Irrigation Season, July - October 2003						
Transfer blanks	2	different creeks	July and Sept	0	- -	- -
Replicate samples	4	1-2 each creek	one each month	0	- -	- -
Fall/Winter Runoff Events, October - December 2003						
Transfer blanks	0	- -	- -	1	unspecified	unspecified
Replicate samples	0	- -	- -	3	unspecified	different events
Spring Intensive, April - June 2004						
Transfer blanks	1	unspecified	unspecified	1	unspecified	unspecified
Replicate samples	3	1 each creek	one each month	2	unspecified	unspecified
FY05	to be determined			to be determined		

The potential for contamination arising from sampling procedures, sample containers, preservation, or transport will be assessed with transfer blanks. Transfer blanks will be prepared in the field by pouring organic-free water, obtained from Manchester Laboratory, into the bottles used for grab sampling and from there into the sample containers for pesticide analysis. The blank water will obtained from Manchester Laboratory. Transfer blanks will be submitted blind to the laboratory.

Selected field samples will be collected in replicate to provide estimates of the total variability in the data (field + laboratory). The replicates will consist of two separate sets of samples collected one after the other. Approximately 10% of field samples will be collected in replicate. Replicate samples will be submitted blind to the laboratory.

Field spikes will be used to determine if there is significant degradation or loss of target compounds between the time of sample collection and analysis. Manchester will provide spiking solutions and pipettes. Three separate spiking solutions each will cover all the OC, OP, and N pesticides being analyzed and one spiking solution each will cover the chlorinated herbicides and carbamates. The spiking will be done on one-gallon or 125 mL (carbamates) sample containers filled with organic-free water by Manchester, 3.0 liters and 125 mL of blank water, respectively. The spiking level will be approximately 0.05 – 1 ug/L. The field spikes will be spaced over the first month of sample collection in coordination with Manchester Laboratory.

Field spiking is a potential source of cross-contamination. Therefore, the spiking will be done after all other samples have been collected. The spiked samples will be placed in separate coolers, double-bagged, and prominently labeled for laboratory staff. Field personnel will wear non-talc nitrile gloves when doing the spiking and take precautions to avoid contaminating other samples and other surfaces.

Laboratory QC elements will include lab control samples (LCS), matrix spikes, matrix spike duplicates (MS/MSD), surrogate spikes, and procedural blanks performed in accordance with the methods and SOPs cited in this QAPP.

Manchester uses spiked blank water as the LCS for pesticide analysis. For sample collections where field spikes are being analyzed, the laboratory will spike the same pesticides at the same level in the LCS.

The frequency of MS/MSDs will be as indicated in Table 4. Extra sample volumes will be collected for the MS/MSDs. The location of the MS/MSD samples will be rotated among stations so as to thoroughly assess the potential for matrix interferences.

No laboratory duplicates are requested for this project.

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Field equipment being used during this project includes an Orion 250A pH meter, a Beckman model RB-5 conductivity bridge, and a precision thermometer. This equipment is maintained by EAP’s instrument technician. The field lead will inspect and test each piece of equipment before taking it into the field. An extra pH meter, conductivity bridge, and thermometer will be taken on each field trip.

For the analytical instrumentation, the testing, inspection, and maintenance will be performed in accordance with the above referenced analytical SOPs and manufacturer's recommendations.

B7. Instrument Calibration and Frequency

The pH meters will be calibrated in accordance with the manufacturer’s instructions at the beginning of each sampling day.

For the analytical instrumentation, calibration will be performed in accordance with the analytical SOP and manufacturer's recommendations.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

No special requirements are needed.

B9. Data Acquisition Requirements

No data will be used from other sources.

B10. Data Management

Data management will be in accordance with the Quality Assurance Manual for the Washington State Department of Ecology Manchester Environmental Laboratory, Volume 2.0.

C. Assessment/Oversight

C1. Assessments and Response Actions

The EAP project manager will observe and assist with the initial sample collection to identify any significant conditions that would adversely affect the quality and usability of the data. The project manager will have the responsibility for initiating and implementing response actions for any problems identified. The project manager will perform a follow-up audit to verify that the response actions were implemented effectively. A minimum of one additional field audit per sampling season will be conducted by the project manager using this QAPP and the method citations.

WSDA personnel will audit field activities at their discretion.

Assessments and response concerning the analytical aspect of the project are addressed in the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0. The information covers examples of conditions indicating out-of-control situations, who is responsible for initiating the corrective actions, and what steps may be taken.

C2. Reports to Management

EAP will prepare annual reports to WSDA. The chemical data will also be available in electronic format. The annual report will include:

- Maps of the study areas showing monitoring stations.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical data.
- Discussion of spatial and temporal patterns observed in the data.
- Recommendations for changes to the following year’s monitoring program.

D. Data Validation and Usability

D1. Data Review, Validation, and Verification Requirements

The data will be reviewed by a qualified analyst at Manchester Laboratory. The laboratory will validate the completeness, correctness, and conformance/compliance of the data set against method and procedural requirements laid out in this QAPP. The laboratory will verify the analytical quality of the data set.

The EAP project manager will be responsible for overall validation and final approval of the data in accordance with project purpose and use of the data. A data quality assessment will be conducted to include:

- Reviewing the DQO, criteria for measurement data, sampling design, and data collection documentation for consistency with the DQO.
- Reviewing the case narratives, calculating basic statistics, and generating graphs of the data to learn about the structure of the data and identify patterns, relationships, or potential anomalies.
- Selecting the most appropriate procedures for summarizing and analyzing the data, based on sampling design, data review, and intended use of the data by WSDA.

D2. Validation and Verification Methods

Manchester Laboratory will validate the data in accordance with the Quality Assurance Manual for the Washington State Department of Ecology Manchester Laboratory, Volume 2.0 and EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, October, 1999.

The EAP project manager will perform the final review and approval of the data prior to transmitting it to WSDA or entering it into EIM as valid. The project manager will review the case narratives and look at field blanks, field replicates, field spikes, surrogate recoveries, LCS recoveries, MS/MSD recoveries, and lab blanks to ensure they are acceptable. The project manager will determine if the data are reasonable and consistent. The project manager will ensure that any anomalies in the data are appropriately documented.

D3. Reconciliation with User Requirements

If the data quality indicators do not meet project requirements outlined in this QAPP, the data may be discarded. The EAP project manager will evaluate the cause of the failure and make decision in consultation with WSDA to discard the data or re-sample if possible. If the failure is tied to the analysis, calibration, and maintenance techniques will be reassessed as identified by the appropriate lab personnel. If the failure is associated with the sample collection, the errors will be pointed out to field personnel.

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Appendix A.
Pesticides and Degradation Products to be Analyzed.

OC Pesticides
Aldrin
alpha-BHC
beta-BHC
delta-BHC
gamma-BHC (Lindane)*
Captafol
Captan*
cis-Chlordane (*alpha*-Chlordane)
trans-Chlordane (*gamma*)
Chlordane (Tech)
2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
4,4'-DDMU
2,4'-DDT
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan Sulfate
Endrin
Endrin Aldehyde
Endrin Ketone
Heptachlor
Heptachlor Epoxide
Hexachlorobenzene
Kelthane (Dicofol)
Methoxychlor
Mirex
cis-Nonachlor
trans-Nonachlor
Oxychlordane
Pentachloroanisole
Toxaphene

OP Pesticides
Azinphos (Guthion) *
Bolstar (Sulprofos)
Carbophenothion

Chlorpyrifos[*]
Demeton-O
Demeton-S
Diazinon[*]
Dimethoate[*]
Disulfoton (Di-Syston)[*]
EPN
Ethion
Ethoprop[*]
Azinphos Ethyl (Ethyl Guthion)
Fenamiphos[*]
Fenitrothion
Fensulfothion
Fenthion
Fonofos
Imidan
Malathion[*]
Merphos (1 & 2)
Methyl Chlorpyrifos
Methyl Parathion[*]
Parathion
Phorate[*]
Ronnel
Sulfotepp

Nitrogen-Containing Pesticides
Alachlor[*]
Ametryn
Atraton
Atrazine[*]
Benefin
Bromacil
Butachlor
Butylate
Carboxin
Chlorothalonil (Daconil)[*]
Chlorpropham
Cyanazine
Cycloate
Di-allate (Avadex)
Diphenamid
Dichlobenil[*]
Diuron[*]
Eptam
Ethalfluralin (Sonalan)
Fenarimol

Fluridone
Hexazinone
Metalaxyl
Metolachlor*
Metribuzin*
MGK264
Molinate*
Napropamide
Norflurazon*
Oxyfluorfen*
Pebulate*
Pendimethalin*
Profluaralin
Prometon (Pramitol 5p)
Prometryn*
Pronamide (Kerb)
Propachlor (Ramrod)
Propargite*
Propazine
Simazine*
Tebuthiuron*
Terbacil*
Terbutryn (Igran)
Treflan (Trifluralin)*
Triadimefon
Triallate
Vernolate

Herbicides
Acifluorfen (Blazer)
Bentazon*
Bromoxynil*
2,4-D*
Dacthal (DCPA)
2,4-DB
Dicamba I*
3,5-Dichlorobenzoic Acid
Dichlorprop
Diclofop-Methyl
Dinoseb
Ioxynil
MCPA
MCPP (Mecoprop)
4-Nitrophenol
Pentachlorophenol
Picloram

2,4,5-T
2,4,5-TB
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
2,4,5-TP (Silvex)
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Trichlopyr*
2,4-Dichlorophenylacetic acid

Carbamates
Aldicarb
Aldicarb Sulfone
Aldicarb Sulfoxide
Baygon (Propoxur)
Carbaryl*
Carbofuran*
3-Hydroxycarbofuran
Methiocarb
Methomyl*
1-Naphthol
Oxamyl (Vydate)
Dioxacarb
Promecarb

*Indicates compound included in the Washington Toxics Coalition lawsuit against the U.S. EPA. The following compounds are also part of the lawsuit but are not part of the analytical methodology for FY03:

1,3-Dichloropropene
Acephate
Bensulide
Coumaphos
Diflubenzuron
Fenbutatin-oxide
Iprodione
Linuron
Methamidophos
Methidathion
Naled
Oryzalin
Paraquat Dichloride
Phosmet
Thiobencarb
Thiodicarb

Appendix B.
Base/Neutral/Acid Organics to be Analyzed.

Acenaphthene
Acenaphthylene
Aniline
Anthracene
Benzidine
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzoic Acid
Benzyl Alcohol
Butylbenzylphthalate
4-Bromophenyl-phenylether
Di-N-Butylphthalate
Caffeine
Carbazole
4-Chloro-3-Methylphenol
4-Chloroaniline
Bis(2-chloroethoxy)Methane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenyl-Phenylether
Chrysene
3B-Coprostanol
Dibenzo(a,h)anthracene
Dibenzofuran
3,3'-Dichldorobenzidine
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitortoluene
1,2-Diphenylhydrazine
Fluoranthene
Fluorene
2-Flurophenol
Hexachlorobenzene
Hexachlorobutadiene

Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isophorone
4,6-Dinitro-2-Methylphenol
1-Methylnaphthalene
2-Methylnaphthalene
2-Methylphenol
4-Methylphenol
Naphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
Nitrobenzene
2-Nitrophenol
4-Nitorphenol
N-Nitroso-Di-N-Propylamine
N-Nitrosodiphenylamine
2,2'-oxybis(1-chloropropane)
Pentachlorophenol
Bis(2-Ethylhexyl)Phthalate
Diethylphthalate
Dimethylphthalate
Di-N-Octyl Phthalate
Phenanthrene
Phenol
Pyridine
Pyrene
Retene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophneol
D4-2-Chlorophenol
1,2-Dichlorobenzene-D4
2-Fluorobiphenyl
D5-Nitorbenzene
D5-Phenol
D10-Pyrene
D14-Terphenyl
Dibenzo(a,j)acridine
Benzo(a,l)pyrene
Dibenzo(a,e)pyrene
Dibenzo(a,i)pyrene
Dibenzo(a,h)pyrene

Appendix C.
Watershed Statistics.

	Watershed Area (acres)	Crop Area (acres)	% Cropped
Snipes Creek	23101	3440	15
Spring Creek	29015	6928	24
Sulphur Creek	98141	34010	35
Satus Creek	42522+	3286	8
Toppenish Creek	190108+	13874	7
Marion Drain	76622	56137	73
Ahtanum Creek	41551+	7395	18
Wide Hollow Creek	37950	8718	23

+watershed is larger than calculated

Spring Creek	Distribution of Crops (%)
Annual	8.1
Apples	20.1
Cherries	2.0
Currant	0.4
Grapes	48.0
Hop	21.3

Snipes Creek	Distribution of Crops (%)
Annual	1
Apples	36
Grapes	37
Hop	20
Soft Fruit	4
Cherries	2

Sulphur Creek	Distribution of Crops (%)
Alfalfa	11.5
Apples	16.2
Asparagus	4.2
Beans	0.1
Cherries	1.2
Corn	18.3
Grapes	35.0
Grass	1.7
Hops	9.2
Mint	1.2
Pears	0.5
Pumpkins	0.2
Sorghum	0.0
Golf Course	0.6
Wheat	0.2

Satus Creek	Distribution of Crops (%)
Alfalfa	4
Asparagus	25
Corn	6
Mint	4
Wheat	60

Toppenish Creek	Distribution of Crops (%)
Alfalfa	36.0
Apples	15.7
Asparagus	5.3
Carrots	0.4
Clover	0.6
Corn	5.2
Fallow	0.8
Grapes	5.6
Grass	6.2
Hops	10.3
Mint	5.6
Pears	2.0
Potatoes	0.4
Squash	0.4
Wheat	5.3

Marion Drain	Distribution of Crops (%)
Alfalfa	4.7
Apples	32.1
Asparagus	2.0
Cherries	1.0
Corn	13.5
Fallow	0.7
Grapes	3.6
Grass	0.5
Hops	24.9
Mint	3.5
Peaches	1.7
Pears	1.1
Peas	0.4
Potatoes	0.3
Squash	0.2
Wheat	9.9

Ahtanum Creek	Distribution of Crops (%)
Alfalfa	1.0
Apples	94.3
Cherries	0.9
Grass	1.3
Pears	1.9
Golf Course	0.6

Wide Hollow Creek	Distribution of Crops (%)
Alfalfa	0.1
Apples	91.8
Cherries	0.9
Grass	0.2
Pears	5.1
Golf Course	1.8